Synopsis

Introduction

Recent advancements in nanotechnology and emerging applications of nanomaterials in various fields have stimulated interest in fundamental scientific research dealing with the size and structure controlled synthesis of nanoparticles. The unique properties of nanoparticles are largely size dependent which could be tuned further by varying shape, structure, and surface properties, etc. The preparation of monodisperse nanoparticles is desirable for many applications due to better control over properties and higher performance compared to polydisperse nanoparticles. There are several methods for the synthesis of nanoparticles based on top-down and bottom-up approaches. The main disadvantage of top-down approach is the difficulty in achieving size control. Whereas, uniform nanoparticles with controllable size could be obtained by chemical methods but most of them are difficult to scale up. Moreover, a separate step of size separation is necessary in order to achieve monodispersity which may lead to material loss. In this context, a post-synthetic size modification process known as digestive ripening is highly significant. In this process, addition of a capping agent to polydisperse colloid renders it highly monodisperse either under ambient or thermal conditions. In addition to size control, digestive ripening is also effective in controlling the structure of nanoparticles in colloidal solution comprising two different elements. Use of co-digestive ripening strategy in conjunction with solvated metal atom dispersion (SMAD) method of synthesis resulted in heterostructures such as core–shell,

alloy, and composite nanoparticles. Despite the versatility of digestive ripening process, the underlying mechanism in controlling size and structure of nanoparticles are not understood to date. The aim of this thesis is to gain mechanistic insight into size control of digestive ripening as well as to investigate structure control in various binary systems.

Objectives

- Study digestive ripening of Au nanoparticles using various alkyl amines to probe the mechanism
- Study co-digestive ripening of binary colloids consisting of two metals, Pd and Cu prepared separately by SMAD method
- Study co-digestive ripening of binary colloids consisting of a metal (Au) and a semiconductor (CdS) prepared separately by SMAD method
- Study vaporization of bulk brass in SMAD reactor and analyze phase, structure, and morphology of various Cu/Zn bimetallic nanoparticles obtained from bulk brass under various experimental conditions

Significant results

In chapter 1, fundamental processes of nanoparticle formation and common synthetic techniques for the preparation of monodisperse nanoparticles are briefly discussed. Chapter 2 presents a mechanistic study of digestive ripening process with regard to size control using Au nanoparticles as a model system. Three long chain alkyl amine molecules having different chain length were used as digestive ripening agents. The course of digestive ripening process was analyzed by UV-visible spectroscopy and transmission electron microscopy. The experimental conditions such as concentration of digestive ripening agent, time, and temperature were found to influence the size distribution of nanoparticles. The average particle size was found to be characteristic of metal-digestive ripening agent combination

which is considered as the optimum size preferred during digestive ripening under a given set of experimental conditions. This study discusses stabilization of optimum sized particles, surface etching, and reversibility in digestive ripening.

Chapter 3 describes the synthesis and characterization of PdCu alloy nanoparticles by co-digestive ripening method. Syntheses of individual Pd and Cu colloids were carried out by SMAD method. Pd nanoparticles obtained using THF as solvent and in the absence of any capping agent resulted in an extended small Pd nanowire network assembly. Morphological evolution of spherical Pd nanoparticles from Pd nanowire network structure was observed with the use of capping agent, hexadecyl amine (HDA) in SMAD method. Co-digestive ripening of Pd and Cu colloids was studied at various temperatures. This study revealed temperature dependent diffusion of Cu atoms into Pd lattice forming PdCu alloy nanoparticles.

Next, co-digestive ripening of a colloidal system comprising a metal and a semiconductor was explored. Au-CdS combination was chosen for this study owing to its interesting photocatalytic properties. Chapter 4 deals with the synthesis of Au and CdS nanoparticles by SMAD method and Au/CdS nanocomposite by co-digestive ripening. CdS nanoparticles of size 4.0 ± 1.2 nm and Au nanoparticles of size 5.6 ± 1.1 nm were obtained as a result of digestive ripening process. Au/CdS nanocomposite obtained by co-digestive ripening was characterized by a matrix-like structure made up of CdS nanoparticles in which Au nanoparticles were embedded. CdS nanoparticles were found to establish an intimate surface contact with Au nanoparticles and the matrix of CdS surrounding Au was developed via aggregation during digestive ripening.

Chapter 5 describes a comprehensive study on various Cu/Zn bimetallic nanoparticles obtained from bulk brass. Vaporization of bulk brass in SMAD reactor led to a dealloying

process and further growth of nanoparticles from phase separated Cu and Zn atoms formed a composite structure. The characterization of Cu/Zn nanocomposite revealed covering of composite surface with Cu resulting in a core-shell structure, Cu/Zn@Cu. Post-synthetic digestive ripening of these core-shell composite particles showed diffusion of Zn atoms to the composite surface in addition to size and shape modification. Annealing of Cu/Zn nanocomposites prepared in THF resulted in α-CuZn alloy nanoparticles via sequential transformation through η-$CuZn_5$, γ-Cu_5Zn_8, and β-CuZn (observed as martensite) phases.